Science Highlights in Advanced Crystallography

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Resonant Diffraction Anomalous Fine Structure (DAFS)

Elemental **identification** at given crystallographic sites

Only at **synchrotron** light sources

\[ f = f^0 + f' + if'' \]

Permits **site-specific** element ID and oxidation state determination

7.09 keV 7.11 keV 7.13 keV 7.15 keV
Resonant Diffraction Anomalous Fine Structure (DAFS)

Elemental **identification** at given crystallographic sites
Only at **synchrotron** light sources

Variable $h\nu = f^0 + f' + if''$

**Permits site-specific** element ID and oxidation state determination

*Fe K-edge:* photoionization of a Fe*(1s)* electron

Bartholomew, Teesdale, Hernandez Sanchez, Malbrecht, Juda…YS Chen, TAB PNAS 2019, 116, 15836
Resonant Diffraction Anomalous Fine Structure (DAFS)

Elemental **identification** at given crystallographic sites
Only at **synchrotron** light sources

\[
f = f^0 + f' + if''
\]

Permits **site-specific** element ID and oxidation state determination

\[\Delta = 17\%\]

\[\Delta = 4\%\]

Resonant Diffraction Anomalous Fine Structure (DAFS)

Elemental *identification* at given crystallographic sites
Only at *synchrotron* light sources

\[ f = f^0 + f' + i f'' \]

Permits *site-specific* element ID and oxidation state determination

Powers, et al. *JACS* 2013, 135, 12289
Identification of specific elements at given crystallographic sites

Proposed the canted beamline would extend the energy range down to 3 keV, providing access to the entire series of $3d \rightarrow 4d$ transition metals, including Sc, Ti, V, K, and Ca, which are not accessible on the existing beamline

**Only at synchrotron light sources**
In-situ crystal diffraction

Environmental Control Cell (ECC)

- Vacuum, gas, solution and humidity

Benedict Group and ChemMatCARS

Structural Dynamics Today

Approaching ‘real time’ structural information about guest and framework solving single crystal structures!
Time Resolved Structural Dynamics

- How do water molecules leave?
  - Stepwise?
  - Simultaneous?
- What is the relationship between compression of a-axis and dehydration?
- Dynamic in situ X-ray Diffraction experiments should address both questions!

Trihydrate (one coordinated water and two ‘free’ water molecules)

Space group $P2_1/c$

- $a = 12.4381 \text{ Å}$
- $b = 7.6827 \text{ Å}$
- $c = 15.8704 \text{ Å}$
- $\beta = 106.1466^\circ$

Anhydrous

Space group $P2_1/c$

- $a = 11.078 \text{ Å}$
- $b = 7.761 \text{ Å}$
- $c = 15.945 \text{ Å}$
- $\beta = 106.829^\circ$
How do water molecules leave?
- Stepwise?
- Simultaneous?

What is the relationship between compression of a-axis and dehydration?

Dynamic in situ X-ray Diffraction experiments should address both questions!
Structural Dynamics Tomorrow: Small Molecule Serial Crystallography

- **What is it?**
  - Technique developed by structural biologists
  - Datasets consist of single images collected from tens or hundreds of thousands of single crystals
  - New sample delivery methods
  - New data analysis methods

- **Why would you do this?**
  - Only method capable of obtaining time-resolved data on:
    - Irreversible processes
    - Applies to process and damage
    - Sub-micron crystals

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